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Oscillatory Indirect Interaction Between Adsorbed Atoms^{*}

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Abstract

The oscillatory part of the indirect interaction between two adatoms on a metal surface, separated by a large distance R , is examined for the jellium as well as for the tight-binding model. The asymptotic form of the interaction is derived from the singularity of its Fourier transform at wave number $q = 2 k_F$. For a substrate with a spherical Fermi surface, the interaction energy is proportional to $\cos(2 k_F R)/R^5$. The fall-off is faster than the corresponding oscillatory interaction between two impurities in the bulk, which varies as $\cos(2 k_F R)/R^3$. For substrates with a partially filled surface band, the interaction energy falls off much more slowly. Under simple assumptions, the interaction behaves as $\cos(2 k_F R)/R^2$. Comparisons are made with the numerical calculations by Einstein and Schrieffer. The experimental results of Tsong on Re atoms adsorbed on W using field-ion microscopy is also discussed.

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1. Introduction

In earlier papers, we examined the substrate-modified dipole-dipole interaction⁽¹⁾ and the phonon-mediated elastic interaction⁽²⁾ due to two atoms,⁽³⁾ A and B, adsorbed on the surface of a metal, and separated by a large distance R. Both of these are non-oscillatory and vary as R^{-3} .

The oscillatory indirect interaction between adsorbed atoms has been discussed earlier by Grimley,⁽⁴⁾ Grimley and Walker,⁽⁵⁾ and Einstein and Schrieffer,⁽⁶⁾ and Tsong⁽⁷⁾ reported experimental evidence for the oscillatory interaction between Re atoms adsorbed on W. These papers will be discussed in Sec. V.

An exact expression for the static density response function $K(\underline{r}, \underline{r}')$ for a sine-wave gas has been derived by Rudnick.⁽⁸⁾ (The electrons are confined to the half-space $z \geq 0$ by an infinite potential.) The response function is given by

$$K(\underline{r}, \underline{r}') = -k_{TF}^2 \pi k_F \left(\frac{1}{R_o^2} j_1(2k_F R_o) + \frac{1}{R_i^2} j_1(2k_F R_i) - \frac{2}{R_o R_i} j_1[k_F(R_o + R_i)] \right), \quad (1.1)$$

where k_F is the Fermi wave number,

$$k_{TF} = \sqrt{\frac{4 Me^2 k_F}{\pi \hbar^2}} \quad \text{is the Thomas-Fermi wave vector,}$$

$$R_o = [(x - x')^2 + (y - y')^2 + (z - z')^2]^{1/2},$$

$$R_i = [(x - x')^2 + (y - y')^2 + (z + z')^2]^{1/2},$$

$$\text{and } j_1(x) = \frac{\sin x}{x} - \frac{\cos x}{x^2}$$

is a spherical Bessel function of first order.

We have expanded this function $K(\underline{r}, \underline{r}')$ for the case where both \underline{r} and \underline{r}' are near the surface and the separation $R = [(x - x')^2 + (y - y')^2]^{1/2}$ is large compared to k_F^{-1} . After some straightforward algebra, one finds the following expansion in inverse powers of R :

$$K(\underline{r}, \underline{r}') = -4k_{TF}^2 \pi k_F^2 \frac{z^2 z'^2 \cos(2k_F R)}{R^5} + O\left(\frac{1}{R^7}\right). \quad (1.2)$$

This is in contrast to the R^{-3} dependence of the Ruderman-Kittel type interaction between two point imperfections in the bulk of a free electron gas. ⁽⁹⁾

In this paper, we also examine the indirect interaction between two adatoms under more general assumptions. In Sec. II, we use the jellium model for the metal surface in which the electrons extend beyond the jellium edge, and in Sec. III, we use the tight-binding model for both the metal and the adatoms. We shall show that the Fourier transform of the interaction energy has a singularity at wave vector $|\underline{q}| = 2k_F$, where \underline{q} is parallel to the substrate surface and $2k_F$ is the appropriate diameter of the Fermi surface, and that this

singularity is responsible for the oscillatory interaction at large distances. If we assume that the metal has a spherical Fermi surface, then we find that the interaction energy is proportional to $\cos(2k_F R)/R^5$. In the vicinity of a surface, the amplitude of the relevant wave-functions tends to zero as R tends to infinity. This weakens the singularity of the response function compared to that for the bulk electron gas, and causes the interaction to fall off more rapidly.

In Sec. IV, we consider the case where the substrate has a partially filled surface band. Virtual excitations and de-excitations of the substrate electrons in the surface band contribute to the interaction energy which falls off much more slowly, so that it will be the dominant part of the interaction between the adatoms when they are far apart. If we assume that the Fermi surface for the energy band is cylindrical, then asymptotically, the interaction falls off as R^{-2} .

II. Interaction Energy: Free Electron Model

We consider a non-interacting electron gas in a jellium background, occupying the space $z \leq 0$. The adatoms A and B, at \underline{r}_A and \underline{r}_B respectively, are represented by an external potential of the form

$$\Delta\varphi(\underline{r}) = \varphi_A(|\underline{r} - \underline{r}_A|) + \varphi_B(|\underline{r} - \underline{r}_B|) . \quad (2.1)$$

The correction to the ground state energy of the electron gas is, by second-order perturbation theory,

$$\Delta E = \sum_i \frac{|\langle i | \Delta \varphi | 0 \rangle|^2}{E_0 - E_i} . \quad (2.2)$$

The mutual interaction between atoms A and B, ΔE_{int} , is obtained by subtracting from (2.2) the corresponding expression in which A and B are infinitely far apart:

$$\Delta E_{\text{int}} = \sum_i \frac{\langle 0 | \varphi_B | i \rangle \langle i | \varphi_A | 0 \rangle}{E_0 - E_i} + \text{c. c.} \quad (2.3)$$

where $|0\rangle$ is the ground state and $|i\rangle$ the excited state of the electron gas.

(a) Electron wavefunction

The normalized ground state $|0\rangle$ and the excited states $|i\rangle$ are Slater determinants of one-electron wavefunctions

$$\Psi_{\tilde{k}}(\tilde{r}) = (4\pi^3)^{-1/2} e^{i\tilde{p} \cdot \tilde{R}} f(z; k_z). \quad (2.4)$$

\tilde{p} and \tilde{R} are two-dimensional vectors

$$\tilde{p} = (k_x, k_y), \quad \tilde{R} = (x, y), \quad (2.5)$$

and $f(z; k_z)$ satisfies the equation (in atomic units),

$$\left(-\frac{1}{2} \frac{d^2}{dz^2} + v_{\text{eff}}(z) - \frac{1}{2} k_z^2 \right) f(z; k_z) = 0, \quad (2.6)$$

where $v_{\text{eff}}(z)$ is the effective potential. ⁽¹⁰⁾ $v_{\text{eff}}(z)$ vanishes in the interior of the metal and rises rapidly to a constant value $\Delta\phi$ outside.

z_0 is a point near the metal surface such that, effectively, $v_{\text{eff}}(z) = 0$ for $z \leq z_0$ (Fig. 1).

We shall consider only small values of k_z , since these give the main contribution to (2.3). In the interior of the metal, we have

$$f(z; k_z) = \sin(k_z z - \gamma(k_z)) , \quad (2.7)$$

where $\gamma(k_z)$ is the phase shift. For $z > z_0$, we can drop the term $\frac{1}{2}k_z^2$ from (2.6) since it is small compared to $\Delta\phi$, and obtain

$$f(z; k_z) = A(k_z) f(z) . \quad (2.8)$$

$A(k_z)$ is chosen so as to match both the phase and the amplitude of the interior function (2.7) at $z = z_0$ and $f(z)$ is the solution to the equation

$$\left(-\frac{1}{2} \frac{d^2}{dz^2} + v_{\text{eff}}(z) \right) f(z) = 0 , \quad (2.9)$$

with the boundary conditions $f(z) = 0$ as $z \rightarrow \infty$ and $f(z) = z + \text{constant}$ for z near z_0 . With this choice of $f(z)$, we find that $A(k_z)$ is equal to k_z , so that, for small k_z and $z \geq z_0$

$$\Psi_{\tilde{k}}(\mathbf{r}) = (4\pi^3)^{-1/2} e^{i\tilde{p} \cdot \mathbf{R}} \tilde{k}_z f(z) . \quad (2.10)$$

The matrix element $\langle i | \varphi_\alpha | 0 \rangle$, where $\alpha = A, B$, $|0\rangle$ is the ground state of the system and $|i\rangle$ the excited state consisting of an electron-hole pair of wave vectors $\tilde{k} = (\tilde{p}, k_z)$ and $\tilde{k}' = (\tilde{p}', k'_z)$ is given by

$$\begin{aligned}
\langle i | \varphi_\alpha | 0 \rangle &= \frac{1}{4\pi^3} \int d^3 \tilde{r} e^{-i\tilde{p}' \cdot \tilde{R}} f(z; k'_z) \varphi_\alpha(\sqrt{|\tilde{R} - \tilde{R}_\alpha|^2 + (z - z_\alpha)^2}) e^{i\tilde{p} \cdot \tilde{R}} f(z; k_z) \\
&= \frac{1}{4\pi^3} e^{iq \cdot \tilde{R}_\alpha} \int_{-\infty}^{\infty} dz f(z + z_\alpha; k_z) f(z + z_\alpha; k'_z) \int d^2 \tilde{R} e^{iq \cdot \tilde{R}} \varphi_\alpha(\sqrt{R^2 + z^2}),
\end{aligned}
\tag{2.11}$$

where

$$q = \tilde{p} - \tilde{p}' \quad . \tag{2.12}$$

The energy denominator in eq. (2.3)

$$E_0 - E_i = -\frac{1}{2} (q^2 + 2\tilde{p} \cdot \tilde{q} + k_z'^2 - k_z^2)$$

vanishes for $\tilde{p} \cdot \tilde{q} = -\frac{1}{2} q^2$ and $k_z = k'_z = 0$, so that the main contribution to (2.3) comes from \tilde{p} , k_z and k'_z near these values. Hence we shall consider only small values of k_z and k'_z and write

$$\langle i | \varphi_\alpha | 0 \rangle = \frac{1}{4\pi^3} e^{iq \cdot \tilde{R}} k_z k'_z I_\alpha(z_\alpha), \tag{2.13}$$

where

$$I_\alpha(z_\alpha) = \int_{-\infty}^{\infty} dz (f(z + z_\alpha))^2 \int d^2 \tilde{R} e^{iq \cdot \tilde{R}} \varphi_\alpha(\sqrt{R^2 + z^2}). \tag{2.14}$$

The mutual interaction between adatoms A and B is then

$$\Delta E_{\text{int}} = \left(\frac{2}{4\pi^3} \right)^2 I_A(z_A) I_B(z_B) \int d^2 \tilde{q} e^{iq \cdot (\tilde{R}_A - \tilde{R}_B)} G(q) + \text{c. c.} \tag{2.15}$$

where the factor 2 takes spin into account and

$$G(q) = - \int_{\substack{p_z^2 + k_z^2 \leq k_F^2 \\ k_z \geq 0}} d^2 p_z dk_z \int_0^{k_0} dk'_z \frac{k_z^2 k'^2_z}{\frac{1}{2}(q^2 + 2k_x q + k_z'^2 - k_z^2)} \quad (2.16)$$

A cutoff k_0 has been introduced in the integral to avoid divergence, but as we shall see later, the precise value of k_0 is immaterial.

(b) Evaluation of the integral

The asymptotic form of the interaction is derived from the singularity of $G(q)$ at $2k_F$. Thus we shall retain only the part of $G(q)$ that is non-analytic at $q = 2k_F$ and drop the remaining part. The singularity of $G(q)$ is very weak. In fact, $G(q)$ and the first three of its derivatives are continuous at $q = 2k_F$ and only the fourth and higher derivatives are singular. In order to extract this singularity more conveniently, we differentiate $G(q)$ with respect to q four times.

For $q > 2k_F$, the denominator is always positive. Differentiating $G(q)$ four times and integrating over dk_y and dk'_z we obtain

$$\frac{d^4}{dq^4} G(q) = -96 \int k_z^2 k'_z{}^2 \left[\frac{8(q + k_x)^4}{(q^2 + 2k_x q + k_z'^2 - k_z^2)^5} - \frac{6(q + k_x)^2}{(q^2 + 2k_x q + k_z'^2 - k_z^2)^4} - \frac{1}{(q^2 + 2k_x q + k_z'^2 - k_z^2)^3} \right] dk_x dk_y dk_z dk'_z$$

$$\begin{aligned}
= -6\pi \int k_z^2 (k_F^2 - k_z^2 - k_x^2)^{1/2} & \left[\frac{5(q + k_x)^4}{(q^2 + 2k_x q - k_z^2)^{7/2}} - \frac{6(q + k_x)^2}{(q^2 + 2k_x q - k_z^2)^{5/2}} \right. \\
& \left. + \frac{1}{(q^2 + 2k_x q - k_z^2)^{3/2}} \right] dk_x dk_z. \quad (2.17)
\end{aligned}$$

The cutoff k_0 is no longer necessary since the integral is now convergent.

For $q \approx 2k_F$, the main contribution to (2.17) comes from $k_x \approx -k_F$ and $k_z \approx 0$. Putting $k_x = P \cos \theta$ and $k_z = P \sin \theta$ and expanding around $\theta = \pi$, the first term of (2.17) becomes

$$\begin{aligned}
& -30\pi \int_0^{k_F} dP \int_0^\pi d\theta (q + P \cos \theta)^4 P^3 \sin \theta \frac{(k_F^2 - P^2)^{1/2}}{(q^2 + 2Pq \cos \theta - P^2 \sin^2 \theta)^{5/2}} \\
& \approx -30\pi \int_0^{k_F} dP (q - P)^4 (k_F^2 - P^2)^{1/2} P^3 \int_0^\infty \frac{u^2 du}{[q^2 - 2Pq + (qP - P^2)u^2]^{5/2}} \\
& \approx -\pi k_F^2 \int_0^{k_F} \frac{(k_F^2 - P^2)^{1/2} dP}{(q - 2P)^2} \\
& = -\pi k_F^4 \int_0^{\pi/2} \frac{\sin^2 \theta d\theta}{(q - 2k_F \cos \theta)^2} \\
& = -\pi k_F^4 \left[\frac{\pi}{4 k_F^{3/2}} (q - 2k_F)^{-1/2} - \frac{\pi}{8 k_F^2} - \frac{1}{4 k_F^2} \right] \quad (2.18)
\end{aligned}$$

for $q \approx 2k_F$. Hence, for $q \approx 2k_F$, the singular term in (2.18) is $-\frac{1}{4}\pi^2 k_F^{5/2} (q - 2k_F)^{-1/2}$. The other two terms in (2.17) give terms which are less singular than the first and can be neglected.

For $q < 2k_F$, we first take the principal value of the integral over dk'_z in (2.16) to obtain

$$G(q) = \int k_z^2 k_o^2 dk_x dk_y dk_z - \frac{\pi}{2} \int_{q^2 + 2k_x q - k_z^2 \geq 0} k_z^2 (q^2 + 2k_x q - k_z^2)^{1/2} dk_x dk_y dk_z. \quad (2.19)$$

Then, differentiating $G(q)$ with respect to q and proceeding as before, we find that the leading term in $(q - 2k_F)$ is also less singular than $(q - 2k_F)^{-1/2}$.

Thus, the most singular term of $G(q)$ is given by

$$\frac{d^4}{dq^4} G(q) = -\frac{1}{4}\pi^2 k_F^{5/2} |q - 2k_F|^{-1/2} \theta(q - 2k_F), \quad (2.20)$$

where

$$\theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \geq 0 \end{cases} \quad (2.21)$$

For large $|R_A - R_B|$, we can evaluate the integral⁽¹¹⁾

$$\int d^2 \tilde{q} e^{i \tilde{q} \cdot (\tilde{R}_A - \tilde{R}_B)} G(q) = -\pi^3 k_F^3 \frac{\cos(2 k_F R)}{R^5} + O\left(\frac{1}{R^6}\right), \quad (2.22)$$

where $R = |\tilde{R}_A - \tilde{R}_B|$, so that the interaction energy is given by

$$\Delta E_{\text{int}} = -\frac{k_F^3}{2\pi^3} I_A(z_A) I_B(z_B) \frac{\cos(2 k_F R)}{R^5}. \quad (2.23)$$

(c) The strength of the interaction

We calculate the interaction energy between two charges, Z_1 at \tilde{r}_A and Z_2 at \tilde{r}_B , on Al, treating the substrate as a jellium, with $r_s = 2$. If we neglect screening, we obtain ΔE_{int}^0 by taking the external potential to be

$$\Delta \varphi^0(\tilde{r}) = \frac{Z_1}{|\tilde{r} - \tilde{r}_A|} + \frac{Z_2}{|\tilde{r} - \tilde{r}_B|} \quad (2.25)$$

To take screening into account, we note that since the interaction energy involves interaction between electron-hole pairs of wave number $q \approx 2 k_F$, the effect of screening can be approximated by using a static surface dielectric function ϵ_S at $q = 2 k_F$, so that

$$\Delta E_{\text{int}} = \frac{\Delta E_{\text{int}}^0}{\epsilon_S}. \quad (2.26)$$

For $r_s = 2$, the bulk dielectric function ϵ corresponding to $q = 2 k_F$ has a value of 1.15, ⁽¹²⁾ only slightly different from 1.

The surface dielectric function ϵ_S is not known at this time but it is clear that it will also differ only by very little from unity. In what follows, we set $\epsilon_S = 1$.

The interaction energy (from eq. (2.23), (2.14), (2.9) and (2.25)) is plotted in Fig. II. For definiteness, we have taken $r_s = 2$, $z_A = z_B = (2 k_F)^{-1}$ ($= 0.52$ atomic units) and $Z_1 = Z_2 = 1$. For other values of z_A and z_B , the amplitude of the interaction is obtained by scaling by the ratio of the product $I(z_A)$ and $I(z_B)$, which are given in Table I.

III. Interaction Energy: Tight-Binding Model

In this section, we deal with a tight-binding, simple cubic semi-infinite solid with a (100) face. The adatoms A and B, each with a single energy level E_0 , sit on top of the substrate atoms at surface sites $\tilde{0}$ and \tilde{n} respectively. The Hamiltonian of the system is taken to be

$$H = H_0 + H_1 + \lambda H_2 . \quad (3.1)$$

H_0 is the Hamiltonian for the solid, and has nearest neighbor matrix elements only, which are denoted by T , so that the bandwidth of the solid is $12 T$, centered at zero energy. H_1 is the Hamiltonian for the adatoms, with eigenvalue E_0 . λH_2 represents the interaction between the adatoms and the solid. Its only non-zero matrix elements

are $V_{A0} = V_{Bn} = V_{0A}^* = V_{nB}^* = V$. λ is treated as a small parameter, but will eventually be taken as unity. Screening is neglected since, as we saw in Sec. II, its effect is small.

To obtain the indirect interaction energy between adatoms A and B, we have to perform a perturbation calculation to fourth-order in λH_2 . More conveniently, we can use the method of canonical transformation, ⁽¹³⁾

$$\tilde{H} = e^{-i\lambda S} H e^{i\lambda S} \quad (3.2)$$

S is chosen so as to remove to lowest order in λ the matrix elements of \tilde{H}_2 which transfer electrons between the adatom and the substrate atoms:

$$H_2 + i[H_0 + H_1, S] = 0, \quad (3.3)$$

or

$$\left. \begin{aligned} \langle l\alpha | S | l'\alpha' \rangle &= -i \frac{\langle l\alpha | H_2 | l'\alpha' \rangle}{E_{l'\alpha'} - E_{l\alpha}} \quad \text{for } l \neq l' \\ \langle l\alpha | S | l\alpha' \rangle &= 0 \end{aligned} \right\} \quad (3.4)$$

and

$$\langle l\alpha | S | l\alpha' \rangle = 0,$$

where $|l\rangle$ and $|l'\rangle$ are eigenstates of H_0 , which are Slater determinants of single-particle eigenstates $|k\rangle$. $|\alpha\rangle$ and $|\alpha'\rangle$ are eigenstates of H_1 and are of the form $|n_A, n_B\rangle$ where $n_A, n_B = 0$ or 1.

With this choice of S , we have

$$\tilde{H} = H_0 + H_1 + \lambda^2 \tilde{H}_2, \quad (3.5)$$

where the relevant matrix element of \tilde{H}_2 is now given by

$$\begin{aligned} \langle \ell' \alpha' | \tilde{H}_2 | \ell \alpha \rangle = & \frac{1}{2} \sum_{\ell'' \alpha''} \langle \ell' \alpha' | H_2 | \ell'' \alpha'' \rangle \langle \ell'' \alpha'' | H_2 | \ell \alpha \rangle \\ & \times \left(\frac{1}{E_{\ell' \alpha} - E_{\ell'' \alpha''}} + \frac{1}{E_{\ell \alpha} - E_{\ell'' \alpha''}} \right) \delta_{\alpha \alpha'}. \end{aligned} \quad (3.6)$$

We have two cases, depending on whether the unperturbed eigenvalue E_0 is greater than or less than the Fermi level E_F . For the case $E_0 < E_F$, eq. (3.6) describes a virtual excitation from the ground state $|\ell, \alpha\rangle$ to the excited state $|\ell'' \alpha''\rangle$, in which the electron on one of the adatoms is transferred to the conduction band above the Fermi level. The state $|\ell', \alpha\rangle$ is formed when another electron in the conduction band below the Fermi level is then transferred to the adatom, creating an electron-hole pair. The situation is similar for the case $E_0 > E_F$.

The single particle eigenstates $|\tilde{k}\rangle$ of H_0 are of the form

$$|\tilde{k}\rangle = \sqrt{\frac{2}{N}} \sum_{\tilde{m}} e^{i\tilde{p} \cdot \tilde{m}} \sin(k_z(m_z + a)) |\tilde{m}\rangle, \quad (3.7)$$

where $|\tilde{m}\rangle$ is a localized wavefunction centered at \tilde{m} . m_z is the component of \tilde{m} perpendicular to the surface, and $m_z = 0$ for surface sites. N is the number of lattice atoms, a is the lattice constant and $\tilde{k} = (\tilde{p}, k_z)$.

By second-order perturbation theory, treating the term $\lambda^2 \tilde{H}_2$ as the perturbation, we have

$$\Delta E_{\text{int}} = \frac{16|V|^4 \lambda^4}{N^2} \sum_{\substack{\tilde{k}', \tilde{k}'' \\ E_{\tilde{k}'} \leq E_F}} \sin^2(\tilde{k}'_z a) \sin^2(\tilde{k}''_z a) e^{i(\tilde{p}' - \tilde{p}'') \cdot \tilde{n} a} \times \left(\frac{1}{E_{\tilde{k}'} - E_0} + \frac{1}{E_{\tilde{k}''} - E_0} \right)^2 \frac{1}{E_{\tilde{k}'} - E_{\tilde{k}''}}. \quad (3.8)$$

When $E_0 = E_F$, eq. (3.8) becomes singular and we have a resonance. This corresponds to virtual transfer of electrons between the adatom and the conduction band, leading to a very strong interaction. If E_0 is not too close to E_F , and E_F is near the bottom or the top of the energy band, so that the Fermi surface is nearly spherical, eq. (3.8) can be evaluated in the same way as (2.16) to give (putting $\lambda = 1$),

$$\begin{aligned} \Delta E_{\text{int}} &= \frac{16|V|^4}{N^2} \frac{(Na^3)^2}{(2\pi)^6} a^4 \text{Re} \int d^3 \tilde{k}' d^3 \tilde{k}'' \left(\frac{1}{E_{\tilde{k}'} - E_0} + \frac{1}{E_{\tilde{k}''} - E_0} \right)^2 \\ &\quad \times \frac{\tilde{k}'_z{}^2 \tilde{k}''_z{}^2 e^{i(\tilde{p}' - \tilde{p}'') \cdot \tilde{n} a}}{\text{Ta}^2 \left[2k_F(k'_x - k''_x) + k'_z{}^2 - k''_z{}^2 \right]} \\ &= \frac{1}{4} \frac{|V|^4}{T^2 (E_F - E_0)^2} \left(\frac{k_F a}{\pi} \right)^3 \frac{\cos(2k_F n a)}{n^5} \times 2T, \quad (3.9) \end{aligned}$$

where na is the distance between adatoms A and B.

Plots of ΔE_{int} for $|V| = T$ and different values of E_F and E_0 , are given in Fig. III. The results of Einstein and Schrieffer⁽⁶⁾ are also given for comparison.

For E_F in the range $-2T$ to $2T$, the Fermi surface intersects the zone boundary and has saddle points. The method used in Sec. II to evaluate the interaction energy would not be valid, because of the different geometry.⁽¹⁴⁾

IV. Interaction Involving Surface Bands

If the substrate has a surface band that is partly filled, virtual excitations and de-excitations of electrons between empty and occupied states in the band due to the presence of the adatoms will contribute to the interaction energy.

We assume that the Fermi surface for the surface band is cylindrical, so that the energy denominator in (2.3) is given by

$$\begin{aligned} E_0 - E_i &= \frac{1}{2m^*} (p^2 - p'^2) \\ &= -\frac{1}{2m^*} (q^2 - 2\tilde{q} \cdot \tilde{p}) , \end{aligned} \quad (4.1)$$

where m^* is the effective mass, \tilde{p} and \tilde{p}' are two-dimensional wave vectors parallel to the surface and

$$\tilde{q} = \tilde{p} - \tilde{p}' . \quad (4.2)$$

The wavefunctions $\Psi(\underline{r})$ are periodic in the x - and y -directions but damped in the z -direction on both sides of the surface.

Analogous to (2.11), the matrix element $\langle i | \varphi | 0 \rangle$ is given by

$$\langle i | \varphi | 0 \rangle = e^{i\mathbf{q} \cdot \underline{R}} V(\mathbf{q}) , \quad (4.3)$$

where $V(\mathbf{q})$ has the same form as (2.11) except that the wavefunctions $f(z; \mathbf{k}_z)$ are replaced by damped waves. As before, the only relevant matrix elements in the summation in (2.3) involve momentum transfer $q \approx 2k'_F$ where k'_F is the Fermi wave number for the surface band, so that $V(\mathbf{q})$ can be replaced by V_0 , evaluated at $q = 2k'_F$. Equation (2.3) then becomes

$$\begin{aligned} \Delta E_{\text{int}} &= \sum_i \frac{\langle 0 | \varphi_B | i \rangle \langle i | \varphi_B | 0 \rangle}{E_0 - E_i} + \text{c. c.} \\ &= 2m^* |V_0|^2 \sum_{\mathbf{q}, \text{spin}} \frac{e^{i\mathbf{q} \cdot \underline{R}}}{-\frac{1}{2}(q^2 - 2\mathbf{q} \cdot \mathbf{p})} \\ &= 2m^* |V_0|^2 \left(\frac{2A}{4\pi} \right)^2 \int d^2\mathbf{q} e^{i\mathbf{q} \cdot \underline{R}} G(\mathbf{q}) , \end{aligned} \quad (4.4)$$

where

$$G(\mathbf{q}) = \int_{|\mathbf{k}| \leq k'_F} d^2\mathbf{k} \frac{1}{-\frac{1}{2}(q^2 - 2\mathbf{q} \cdot \mathbf{p}_x)} , \quad (4.5)$$

A is the surface area of the substrate and the factor 2 takes spin into account. As in Sec. II, we differentiate $G(\mathbf{q})$ with respect to q and

evaluate the leading term in $(q - 2k'_F)$. We find that the most singular term is given by

$$\frac{d}{dq} G(q) = \frac{\pi}{2} k'_F{}^{-1/2} |q - 2k'_F|^{-1/2} \theta(q - 2k'_F), \quad (4.6)$$

so that⁽¹¹⁾

$$\int d^2 \underline{q} e^{i \underline{q} \cdot \underline{R}} G(q) = -2\pi^2 \frac{\cos(2k'_F R)}{R^2}, \quad (4.7)$$

and

$$\Delta E_{\text{int}} = - \frac{m^* |V_0|^2 A^2}{\pi^2} \frac{\cos(2k'_F R)}{R^2}. \quad (4.8)$$

The interaction falls off like R^{-2} , as compared to the R^{-5} behavior for the bulk band. Thus, when a surface band is present and the Fermi level lies inside the band, its contribution to the interaction will dominate at large distances.

To determine the magnitude of the interaction, we need the value of V_0 . We assume that the wavefunction $\Psi(\underline{r})$ is periodic in x and y and damps exponentially away from the surface. Since typically the surface wavefunction damps much more quickly on the vacuum side, we just cut it off on this side for simplicity. The normalized wavefunction is approximated by

$$\Psi(\underline{r}) = \left(\frac{2K}{A}\right)^{1/2} e^{i \underline{p} \cdot \underline{R}} e^{Kz} \theta(-z), \quad (4.9)$$

where K is a positive constant. For a bare charge at $\underline{r} = (0, z_0)$ we have

$$\begin{aligned}
 V(\underline{q}) &= \frac{2K}{A} \int_{z \leq 0} e^{i\underline{q} \cdot \underline{R}} e^{Kz} (R^2 + (z - z_0)^2)^{-1/2} d^2R dz \\
 &= \frac{2K}{A} 2\pi \int_{-\infty}^0 dz e^{2Kz} \int_0^{\infty} J_0(qR) [R^2 + (z - z_0)^2]^{-1/2} R dR \\
 &= \frac{4\pi K}{A} \int_{-\infty}^0 e^{2Kz} q^{-1} e^{-q|z_0 - z|} dz \\
 &= \frac{4\pi K}{Aq} \frac{e^{-qz_0}}{2K + q} .
 \end{aligned} \tag{4.10}$$

At $q = 2k'_F$, we have

$$V_0 = \frac{\pi K}{A} \frac{e^{-2k'_F z_0}}{k'_F (k'_F + K)} . \tag{4.11}$$

If k'_F is sufficiently large, we may neglect screening as in Sec. II, so that the interaction energy is given by

$$\Delta E_{\text{int}} = -\frac{m^*}{k'^2_F} \frac{e^{-4k'_F z_0}}{(1 + (k'_F/K))^2} \frac{\cos(2k'_F R)}{R^2} . \tag{4.12}$$

This is shown in Fig. IV, with $r_s = 2$ and $z_0 = (2k'_F)^{-1}$ as in Fig. II.

For simplicity, we have taken $m^* = 1$, $k'_F = k_F$ and $(k'_F/K) = 1$.

V. Discussion

Grimley⁽⁴⁾ has derived expressions for the indirect interaction between chemisorbed atoms on bcc and fcc crystal surfaces. Assuming that the Fermi surface is spherical, he obtained two cases, depending on the direction of the vector \underline{R} joining the surface sites to which the adatoms are bonded. In the critical direction, i. e. $\underline{R} \cdot \underline{\tau}_0 = 0$, where $\underline{\tau}_0$ is one of the three primitive translation vectors which is an element of symmetry lost in going from the infinite to the semi-infinite crystal, he obtained an oscillatory interaction that varies as R^{-5} . In other directions, he had again an oscillatory interaction, but varying as R^{-3} . We have rederived his formulas for the interaction energy but found that it varies as R^{-5} for all directions of \underline{R} , in agreement with the result obtained in Sec. II.

Einstein and Schrieffer⁽⁶⁾ calculated the indirect interaction between adatoms on "cubium" for various values of the parameters V , E_F and E_0 . They found the interaction to be oscillatory, and over their range of calculation they fitted it by an exponential form. They also conjectured that asymptotically the interaction amplitude should vary as R^{-5} , but felt that the asymptotic power behavior was not applicable to the relatively small separations they considered.

Our own theory does indeed yield an R^{-5} behavior and we find this asymptotic form fits the numerical results of Einstein and Schrieffer rather well. Some of their results are shown in Fig. III.

The agreement with the present work is very good in one case, and somewhat worse in the other. The reason is presumably that in the second case, the Fermi surface is quite anisotropic, and replacing it by a spherical surface is not a very good approximation.

Tsong, ⁽⁶⁾ using field ion microscopy, observed that the interaction between Re atoms on the (110) face of W is oscillatory, with a period of about 5 Å, and falling off slowly with distance, approximately as R^{-1} . The interaction can be fitted by an expression of the form

$$\Delta E_{\text{int}} = -C \frac{\cos(\Delta k_o R)}{|R|} \quad (5.1)$$

with $C = 0.95 \times 10^{-2}$ and $\Delta k_o = 0.665$ atomic units. Because of the complexity of the W Fermi surface, we have not attempted a detailed calculation for this system. We wish, however, to make the following observations which we believe to be relevant for this system.

The W Fermi surface consists of an electron "jack" at the center of the Brillouin zone and hole "octahedra" at the corners H, with portions of rather flat, parallel faces normal to the (111) and equivalent directions, approximately $\Delta k = 1.0 \text{ Å}^{-1}$ apart. ⁽¹⁵⁻¹⁷⁾ For virtual excitations of the substrate electrons of wave vector \vec{q} in the ($\bar{1}11$) direction (parallel to the substrate (110) face), these flat faces provide large regions around the Fermi surface for which the energy denominator in (2.3) is nearly zero, and hence give the major

contribution to the interaction energy.

We perform a model calculation with a Fermi surface defined by two exactly parallel planes, Δk apart, perpendicular to the $(\bar{1}11)$ direction (taken as the x-direction). The zone boundaries in the other two directions are adjusted so as to give the correct volume in k-space. This gives a rectangular box of dimensions $\Delta k \times k_o \times k_o$, with $\Delta k = 1.0 \text{ \AA}^{-1}$ and $k_o \approx 0.69 \text{ \AA}^{-1}$. The energy denominator in (3.8) is given by $(k_x^2 - k_x'^2)/2m^*$ where m^* is the effective mass. After integrating over k_z and k_z' , (3.8) becomes

$$\begin{aligned} \Delta E_{\text{int}} &= - \frac{4|V|^4 a^6}{(2\pi)^6} \cdot \frac{4}{(E_F - E_o)^2} \cdot 2m^* k_o^2 \int dk_x dk_y dk_y' dk_x' \frac{e^{iq \cdot R}}{q(q - 2k_x)} \\ &= - \frac{|V|^4 a^6 m^* k_o^2}{2\pi^6 (E_F - E_o)^2} \left(\frac{2 \sin \frac{1}{2} k_o y}{y} \right)^2 \int_{-\infty}^{\infty} \frac{1}{2q} \ln \left| \frac{q + \Delta k}{q - \Delta k} \right| e^{iqx} dq \\ &= - \frac{|V|^4 a^6 m^* k_o^2}{2\pi^6 (E_F - E_o)^2} \left(\frac{2 \sin \frac{1}{2} k_o y}{y} \right)^2 \frac{\pi}{\Delta k} \frac{\cos(\Delta k x)}{|x|}. \quad (5.2) \end{aligned}$$

The pair correlation function for the adatoms is given by

$$g(R) = \exp[-\Delta E_{\text{int}}(R)/k_B T]. \quad (5.3)$$

At high temperature ($k_B T \gg \Delta E_{\text{int}}(R)$) the spatial dependence of the interaction energy can be obtained by averaging (5.2) over all angles. Since ΔE_{int} is proportional to $(xy)^{-1}$, we expect that the angular

average should vary as R^{-3} .

At low temperature, the adatoms are "frozen" at sites of minimum energy, corresponding to $y = 0$ and $\cos(\Delta kx) = 1$. Thus,

$$\begin{aligned}\Delta E_{\text{int}} &= - \frac{|V|^4 a^6 m^* k_o^4}{2\pi^5 (E_F - E_o)^2 \Delta k} \frac{\cos(\Delta kx)}{|x|} \\ &= -C' \frac{\cos(\Delta kx)}{|x|} .\end{aligned}\quad (5.4)$$

This has the same form as (5.1), falling off as $|x|^{-1}$ and with a period of oscillation given by $(2\pi/\Delta k) = 6.3 \text{ \AA}$, compared to the observed period of 5 \AA .

The value of C' in (5.4) can be estimated as follows. The substrate, which is simple cubic, is assumed to have the same density as W. Since W is bcc, with lattice constant $= 3.16 \text{ \AA}$, this gives

$$a = 3.16 \text{ \AA} \times 2^{-1/3} = 2.51 \text{ \AA} . \quad (5.5)$$

$m^* \approx 1$ ⁽¹⁷⁾ and $k_o \approx 0.69 \text{ \AA}^{-1}$. The value of $(E_F - E_o)$ is determined by assuming that the energy band of W is formed by the broadening of the 5d electrons, with a bandwidth $W_b = 12 \text{ T} = 10.5 \text{ eV}$, ⁽¹⁷⁾ centered at the 5d atomic level. Since there are four 5d electrons in W, E_F is at 0.35 T below the center of the band. E_o is assumed to be at the 5d level of atomic Re. The 5d levels of

W and Re are at -0.684 and -0.781 Rydberg respectively.⁽¹⁸⁾

These give $(E_F - E_O) = 0.71 \text{ eV}$ (see Fig. V). To obtain a value of $C' = 0.95 \times 10^{-2} \text{ a.u.}$ as in (5.1), we need $V = 1.57 \text{ eV} = 1.8 \text{ T}$.

This is quite reasonable, in view of the fact that Einstein and Schrieffer estimated that V/T be roughly in the range of 3 to 5 for most chemisorption systems.

In Tsong's experiment, the interaction energy is of the order of 30 meV ($\sim 350^\circ\text{K}$) and the experiment was performed at 320°K , so that the temperature is in the intermediate range. Neither of the extreme cases considered above is therefore applicable, but the experimental observations appear to be qualitatively consistent with the effects discussed in this paper.

Acknowledgment

We would like to thank Dr. T. L. Einstein for furnishing us with unpublished results of the calculation of indirect interaction between adatoms.

References

1. W. Kohn and K. H. Lau, Solid State Commun. 18, 553 (1976).
2. K. H. Lau and W. Kohn, Surf. Sci., to be published.
3. This applies to both atoms and molecules. For brevity, we shall use the word atoms.
4. T. B. Grimley, Proc. Phys. Soc. (London) 90, 751 (1967); 92, 776 (1967).
5. T. B. Grimley and S. M. Walker, Surf. Sci. 14, 395 (1969).
6. T. L. Einstein and J. R. Schrieffer, Phys. Rev. B7, 3629 (1973), and private communications.
7. T. T. Tsong, Phys. Rev. Letters 31, 1207 (1973).
8. J. Rudnick, Phys. Rev. B5, 2863 (1972).
9. M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).
10. N. D. Lang and W. Kohn, Phys. Rev. B1, 4555 (1970).
11. M. J. Lighthill, "An Introduction to Fourier Analysis and Generalized Functions (Cambridge University Press, Cambridge, England, 1958).
12. P. Vashishta and K. S. Singwi, Phys. Rev. B3, 875 (1972).
13. For example, see C. P. Slichter, "Principles of Magnetic Resonance" (Harper and Row, New York, 1963), Appendix D.
14. It appears that the shape of the Fermi surface is the determining factor for the spatial dependence of the interaction energy. In the case of saddle points, preliminary calculations indicate

that the interaction falls off less rapidly, probably as R^{-4} .

Two other special shapes of the Fermi surface are discussed in Secs. IV and V.

15. W. M. Lomer, Proc. Phys. Soc. (London) 80, 489 (1962);
84, 327 (1964).
16. W. M. Walsh, Jr. and C. C. Grimes, Phys. Rev. Letters 13,
523 (1964).
17. L. F. Mattheiss, Phys. Rev. 139, A1893 (1965).
18. F. Herman and S. Skillman, Atomic Calculations (Prentice
Hall Inc., 1963).

Table I. The factor $I(z)$ in the matrix element $\langle i | \varphi^0 | 0 \rangle$

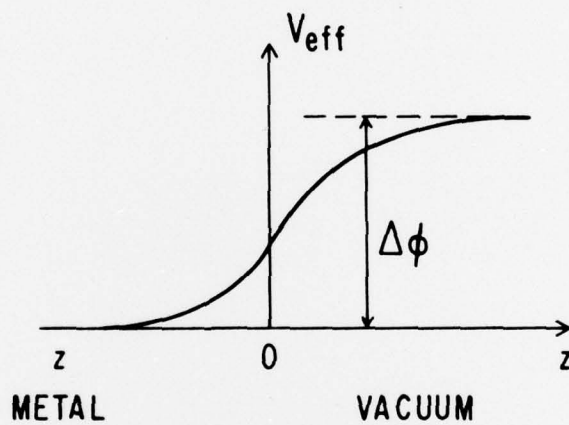
for $r_s = 2$

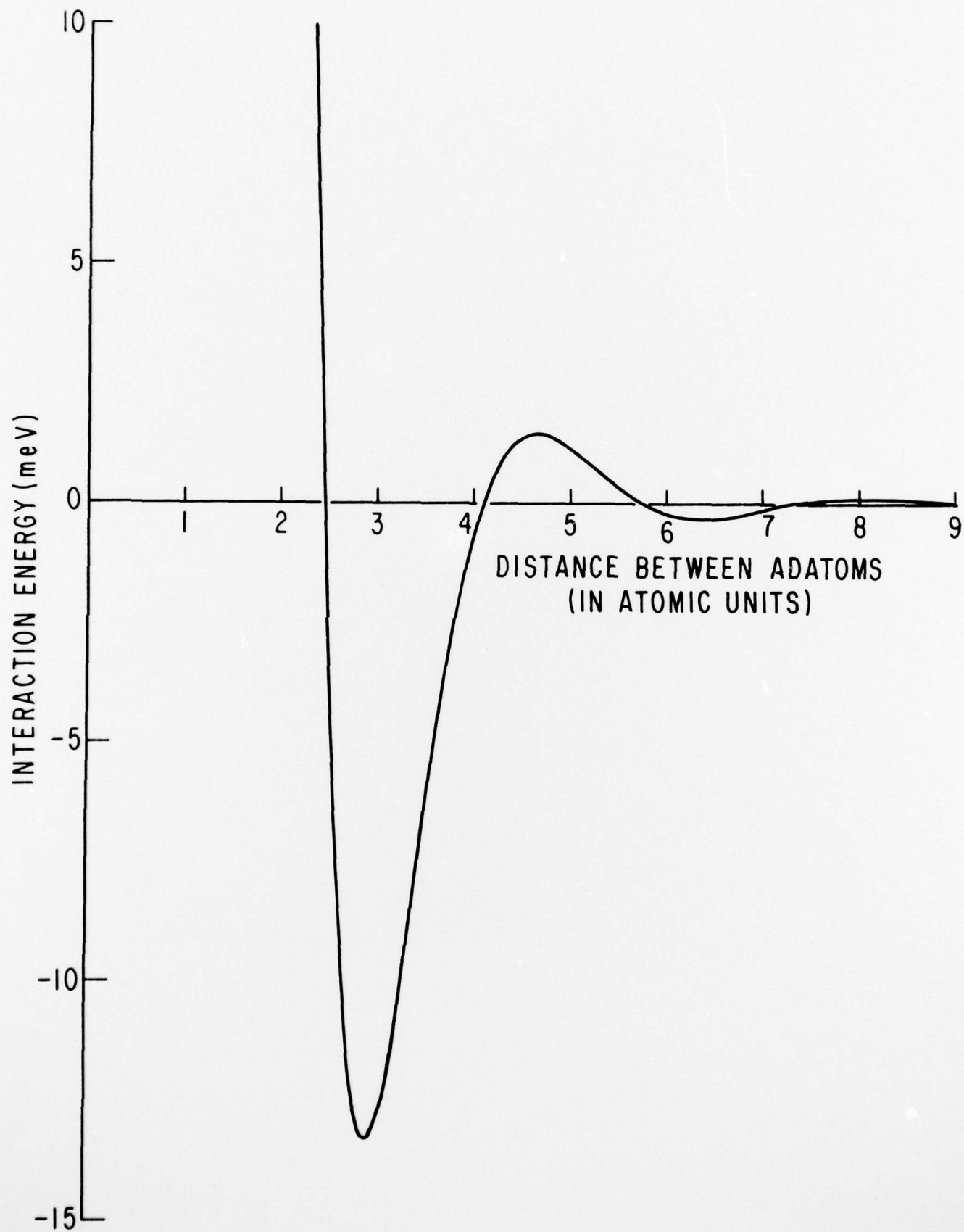
z (in units of $1/2 k_F$)	-1	0	1	2	3	4
$I(z)$ (in atomic units)	8.727	4.882	3.060	1.232	0.5677	0.2513

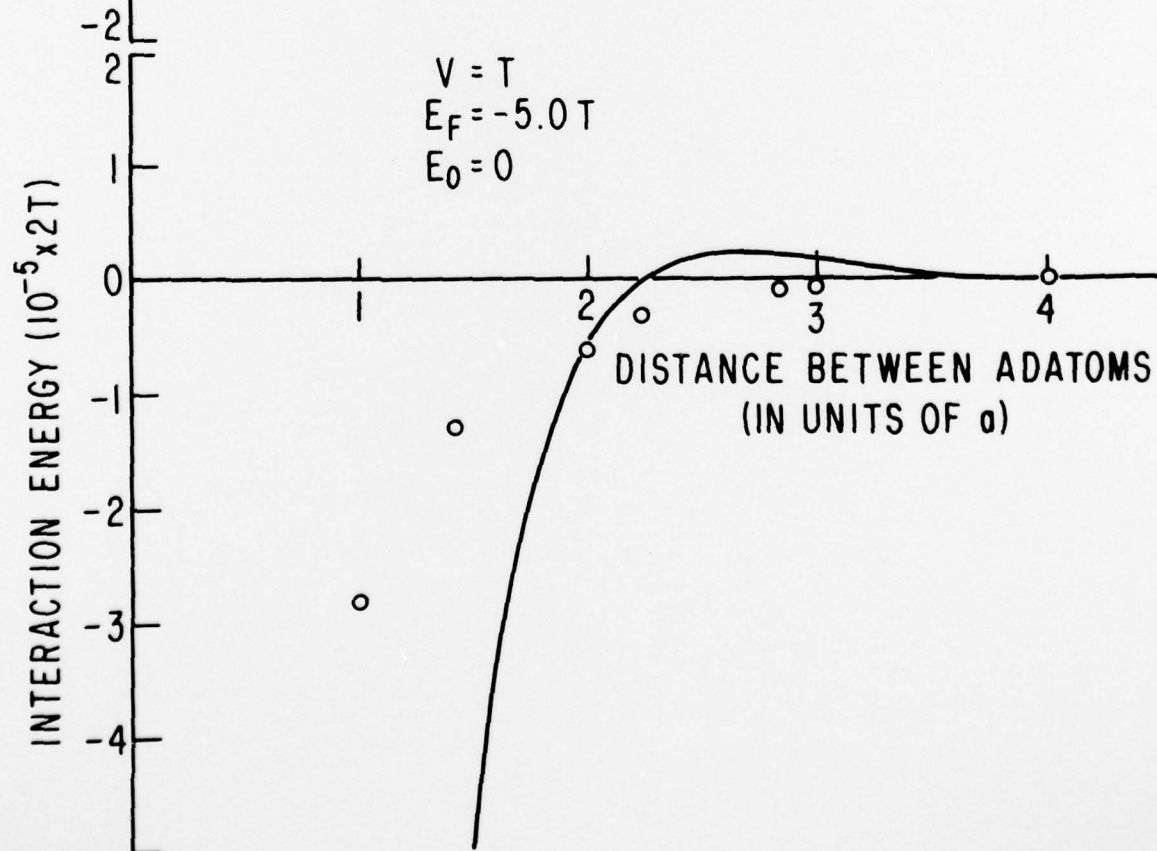
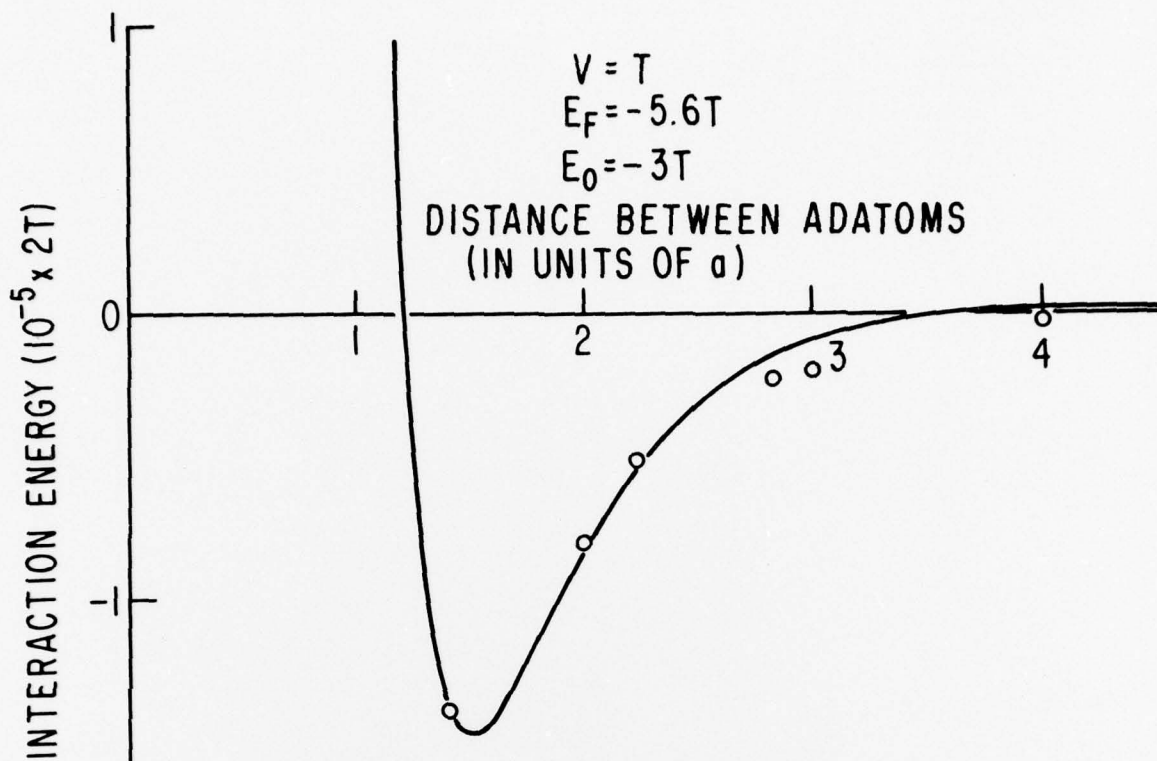
z is measured from the jellium edge, with the jellium on the left.

FIGURE CAPTIONS

- Fig. I Effective one-electron potential v_{eff} (jellium model;
 $r_s = 2$).
- Fig. II Interaction energy between two bare charges near the jellium
surface ($r_s = 2$). The charges are at a distance $(2k_F)^{-1}$ from
the jellium edge.
- Fig. III Comparison of the interaction energy in the tight-binding
model with the calculations of Einstein and Schrieffer
(open circles).
- Fig. IV Interaction energy involving surface bands.
- Fig. V Schematic diagram for the energies in the Re/W system.
All energies are in eV.







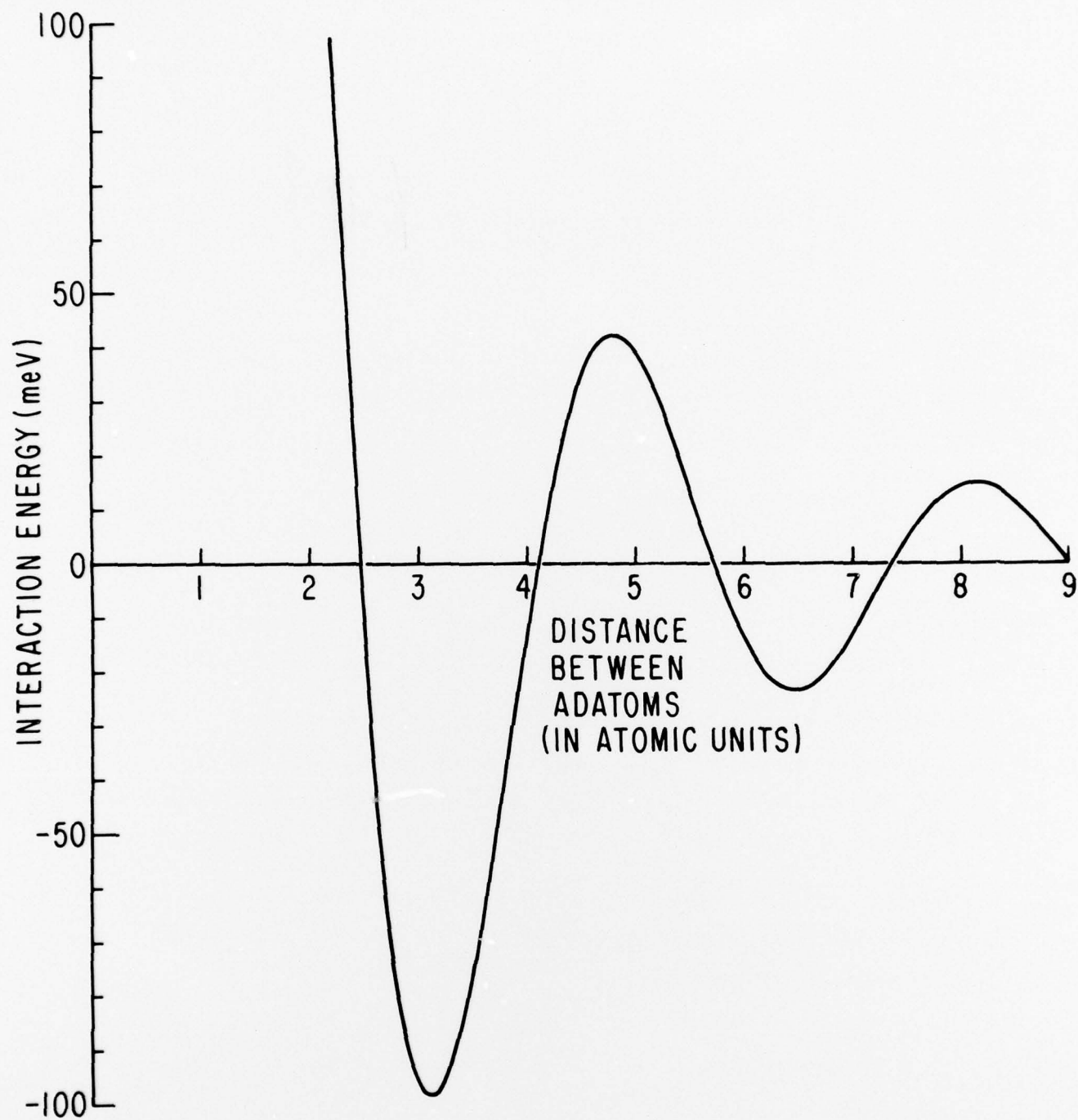


FIGURE IV

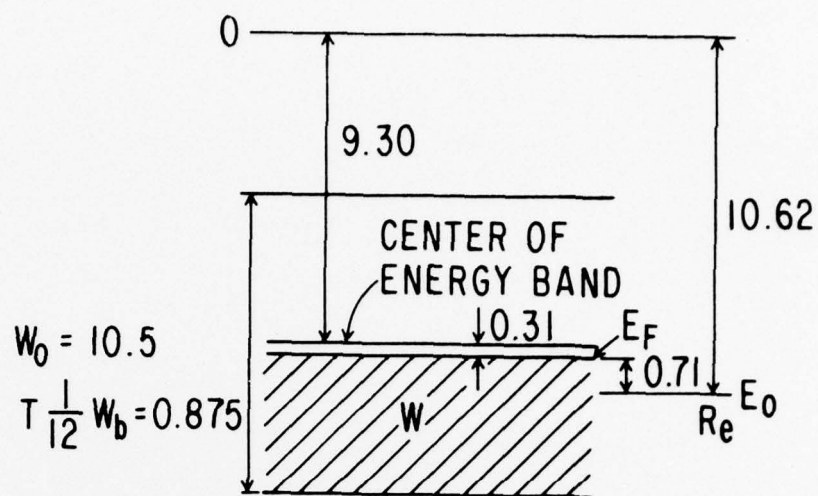


FIGURE V

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cont → Under simple assumptions, the interaction behaves as $\cos(2k_F R)/R^2$. Compari-
sons are made with the numerical calculations by Einstein and Schrieffer.
The experimental results of Tsong on Re atoms adsorbed on W using
field-ion microscopy are also discussed.

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